# REDUCING RELIANCE on CRITICAL MATERIALS

*Livermore researchers support efforts to limit the need for rare-earth elements in U.S. clean-energy technologies.*

HIGH-TECHNOLOGY products, from car motors to fluorescent lighting, often rely on small amounts of scarce raw materials that possess key properties, such as strength, thermal resistivity, and magnetism. No easy substitutes exist for these so-called critical materials, and as a result, demand for them can at times exceed available supply. Indeed, shortages of critical materials can impair entire industries and prevent the development and implementation of new products.

Critical materials include a group of related elements called rare earths, which traditionally include the lanthanide series of elements in the periodic table as well as scandium and yttrium (see the box on p. 7). Rare earths are essential to high-performance magnets and magnetic powders, catalysts, metallurgical additives, polishing powders, phosphors, glass additives, and ceramics used in a variety of industries, including health care, computer, automotive, communications, and optics to name a few. For example, at Lawrence Livermore's National Ignition Facility— the world's largest laser—optics made from ultrapure glass doped with neodymium atoms amplify laser light to the extremely high energies required for experiments.

Many rare-earth elements are also considered critical materials for the U.S

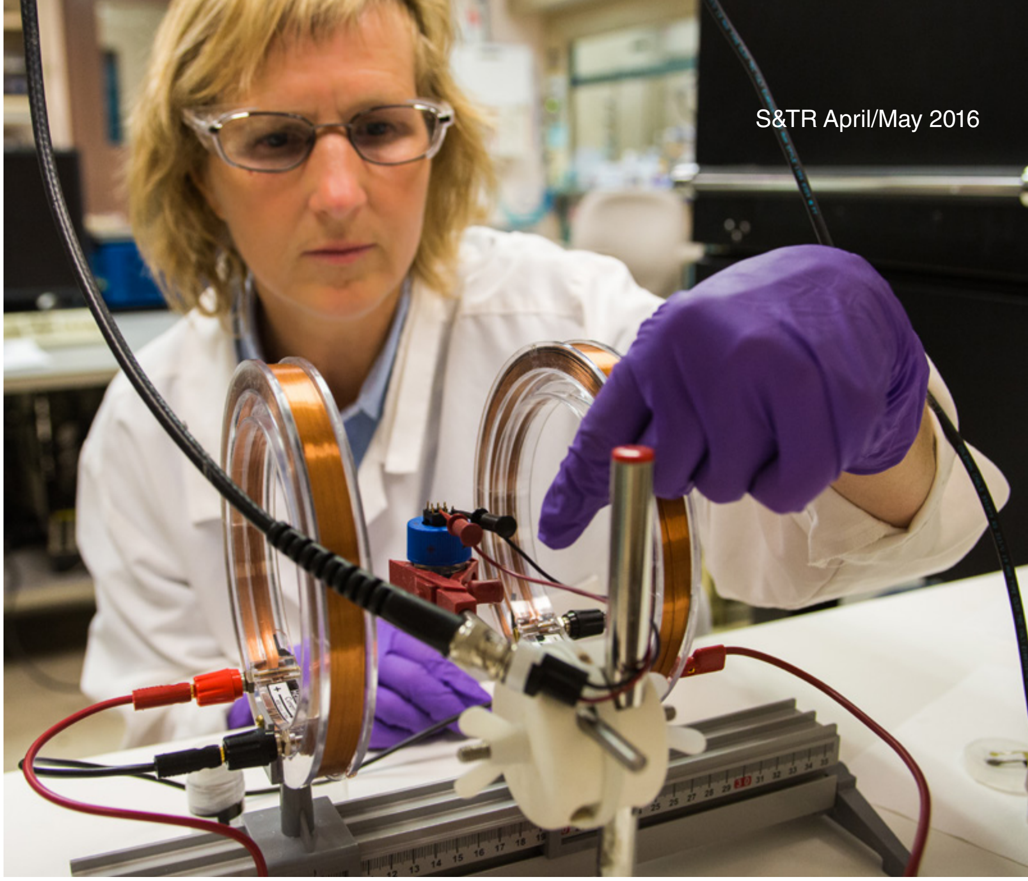
clean-energy industry. Hybrid-electric vehicles, fluorescent lights, large wind turbines, and other clean-energy products all rely on small quantities of rare earths. The Department of Energy's (DOE's) Critical Materials Institute (CMI) was established, in part, to assure supply chains for these precious commodities, thereby enabling innovation in U.S. manufacturing and enhancing the nation's energy security. Established in 2013 with help from Livermore materials scientists, CMI is one of DOE's four Energy Innovation Hubs and is headquartered at Ames Laboratory in Ames, Iowa. A particular focus of CMI is to address the materials criticality issues

Many rare-earth elements are essential to the nation's clean-energy industry. Europium, a rare earth that has the same relative hardness as lead, is used to create fluorescent lightbulbs. With no proven substitutes, europium is considered a critical material to the clean-energy economy. (Photo courtesy of Ames Laboratory.)

associated with five of the rare-earth elements: dysprosium, terbium, europium, neodymium, and yttrium.

CMI-sponsored research is conducted at national laboratories, universities, and U.S. companies. Lawrence Livermore physicist Eric Schwegler, who coordinates CMI-funded research at the Laboratory, notes that rare-earth research has implications for national security and economic vitality. More than 95 percent of rare earths are mined outside the United States. Occasional export restrictions by rare earth–producing nations have prompted concern about the effects a shortage could have on the U.S. clean-energy industry.

CMI is working to reduce the nation's dependence on rare earths through three research focus areas: diversifying supply, developing substitutes, and reuse and recycling. This work is further enhanced by cross-cutting research initiatives that range from establishing new additive-manufacturing technologies to conducting economic analyses of potentially new critical materials. Schwegler says, "Livermore's work for CMI has established the Laboratory's expertise in rare-earth materials synthesis, characterization, and modeling and has contributed to its mission of safeguarding energy security."



Laboratory materials scientist Christine Orme is helping develop exchange spring magnets—objects that are twice as strong, contain half the required rare-earth content, and operate more effectively at higher temperatures than existing permanent magnets. Such technology could drive design of smaller, lighter, and more efficient motors for cars and wind turbines. (Photo by Lanie L. Rivera.)

## A More Varied Supply

Despite their name, rare-earth elements (with the exception of promethium) are found in relatively high concentrations across the globe. However, they seldom occur in easily exploitable deposits because of their geochemical properties. Schwegler adds that rare earths are chemically very similar and thus are generally found mixed together and are difficult to separate. In addition, the lighter rare-earth elements, such as cerium, are often present in greater concentrations than the heavier elements.

To better diversify supply, one strategy under consideration is finding novel applications for rare-earth materials that are relatively abundant but less used. Cerium, for example, is often discarded as a byproduct in the separation and extraction of the more valuable rare earths. If new, significant applications could be found for cerium, the economics of mining rare earths that occur in smaller concentrations could change considerably.

A promising research avenue takes advantage of cerium's low demand to explore the element's suitability as an alloying agent. Currently, no low-cost aluminum alloys have been developed that can operate at elevated temperatures while maintaining the mechanical properties needed for high-performance automotive and aerospace applications. "By combining 10 percent cerium with aluminum and perhaps other elements, we could make stiff, lightweight materials for creating engines that operate at higher temperatures," says Livermore physicist Scott McCall. A high-performance aluminum alloy would enable design of higher efficiency internal combustion engines and lighter drivetrains, thereby improving fuel economy.

McCall is working with colleagues at Oak Ridge National Laboratory and CMI's strategic partner Eck Industries, Inc. of Manitowoc, Wisconsin. They are developing alloys containing cerium, along with appropriate techniques to efficiently manufacture them. Livermore researchers are testing the most promising alloys. "If the tests prove successful, the alloys could trigger a huge demand for cerium," says McCall. Early tests of aluminum alloys with cerium concentrations of 6 to 16 percent have proven that the material is castable and remains strong at room temperature.

## Bring in the Replacements

Livermore researchers are also searching for rare-earth substitutes in magnets used in automobiles, especially hybrid-electric cars. Developed in the 1970s and 1980s, rare earth–based magnets are the strongest type of permanent magnets available. They are found in the more than 40 electric motors and actuators that control various vehicle devices from windshield wipers to speakers. In hybrid-electric cars, rare-earth magnets are part of the vehicles' regenerative braking system. These magnets are also found in lightweight motors for compact computer hard drives and even powerful hand tools. Large, megawatt-scale wind turbines contain approximately 1,000 kilograms of magnets, of which 25 percent by weight are made from rare earths.

Many of these magnets contain neodymium and the expensive rare earth dysprosium. "We want to make these motors cheaper and smaller while using fewer rare-earth elements," says McCall. He is working on a new class of magnet that offers high magnetic coercivity (ability to withstand an opposing external magnetic field without demagnetizing) and high magnetic remanence (the magnetization remaining when the magnetizing field is removed). Other team members include Jonathan Lee, Sarah Baker, Christine Orme, Joshua Kuntz, and Tony Van Buuren.

Rare-earth magnets, such as those made from neodymium–iron–boron or samarium–cobalt alloys, are hard magnetic materials that have high coercivity but only modest remanence. In theory, if these hard

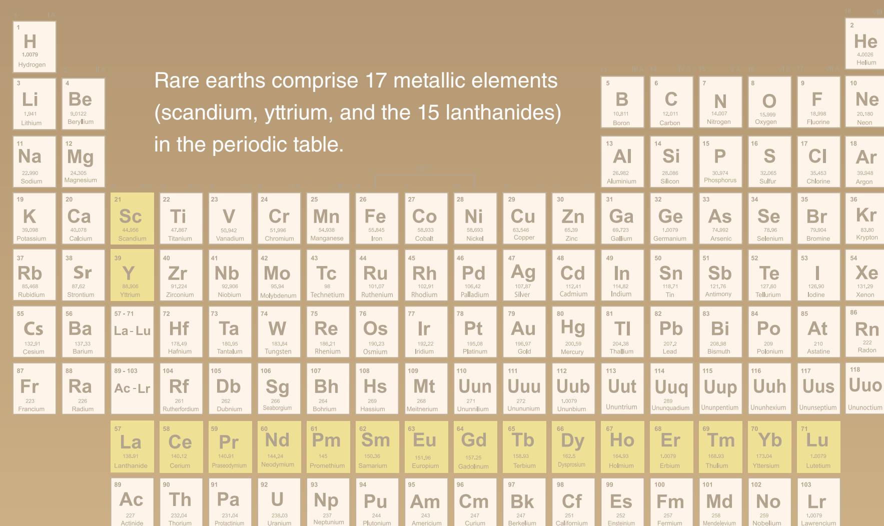
### Rare Earths Have Special Properties

The rare earths comprise 17 metallic elements in the periodic table: scandium, yttrium, and the 15 lanthanides (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium). Scandium and yttrium are considered rare-earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar properties. Used in various technologies from computer hard drives to speakers, rare earths are also essential for U.S. competitiveness in the global clean-energy industry.

Despite their name, rare-earth elements (with the exception of promethium) are found throughout the world. Cerium is particularly plentiful, about as abundant as copper. However, most rare-earth production is concentrated in China. A growing concern exists among scientists and high-technology industries regarding the future supply of five rare-earth elements—dysprosium, terbium, europium, neodymium, and yttrium. Shortages of these materials could affect clean-energy development in the coming years. For example, the largest wind turbines require very powerful neodymium–iron–boron magnets.

The atomic number of each rare earth is exactly one more or one less than its neighboring element along the periodic table. The nominal increase is the result of the successive addition of an electron to a material's 4f electron shell. Understanding the behaviors of these electrons is therefore central to determining how rare-earth elements produce the properties they confer to products. Better theoretical models for f-shell electrons, validated by experiment, are needed to accelerate the discovery and design of new products containing rare earths. In addition, studies of rare earths can provide insight into the properties of actinide elements, which have similar properties and are important for stockpile stewardship research.

When alloyed with other metals, rare earths provide enhanced magnetism, strength, thermal resistance, and other properties. Several rare-earth elements confer material properties that cannot be provided by anything else. For example, neodymium and dysprosium are used in high-strength magnets found in hard drives, speakers, and cars, all of which benefit from higher efficiency and smaller-size magnets.



Rare earths comprise 17 metallic elements (scandium, yttrium, and the 15 lanthanides) in the periodic table.

materials could be interspersed with a soft magnetic material that has high magnetic remanence, the resulting magnet could be twice as strong, contain half the required rare-earth content, and operate more effectively at higher temperatures. Called exchange spring magnets, these objects could drive design of smaller, lighter, and more efficient motors for cars and wind turbines.

“The exchange spring magnet idea has been around since the early 1990s,” says McCall. However, their manufacture has posed significant challenges because the hard material must be distributed at the nanoscale within the soft material matrix. Additive-manufacturing techniques have made fabricating the magnets more feasible. In collaboration with Brown University and General Electric (GE), Livermore scientists are showing how hard and soft magnetic materials can be put down in a checkerboard array using electrophoretic deposition and nanomanufacturing technology. McCall says, “It’s a very promising technique.”

Exchange spring magnets could be commercially available within three to four years after laboratory demonstration. The development team is aiming to produce a prototype for testing by late 2016. Economists see a potential $10 billion market for these magnets. According to McCall, the market for high-strength permanent magnets is so large that even small improvements in magnet strength or reductions in the quantity of rare-earth elements required could save hundreds of millions of dollars annually.

### Modeling Material Alternatives

In a separate project, physicist Patrice Turchi is combining quantum-mechanical simulations and thermodynamic modeling to estimate the phase stability, magnetism, and other properties of potential rare-earth alloys for hard magnet and structural applications. The effort takes advantage of progress in computational materials modeling and Lawrence Livermore’s vast supercomputing resources to optimize design and development of new materials.

Turchi and his team are developing a materials design simulator to accelerate the search for replacements to rare earths or rare-earth alloys that provide the same or enhanced materials stability and performance. Turchi says, “We want to find the optimum proportion of elements that will produce alloys with the best magnetic properties in the case of hard magnet applications, or mechanical properties in the case of structural materials applications.”

By combining the team’s modeling efforts with available experimental data, Turchi and his colleagues Per Söderlind, Alexander Landa, Aurélien Perron, and Vincenzo Lordi can validate quantum-mechanical simulations of rare earths and build a series of validated databases that include the thermodynamic and magnetic properties of rare earth–based materials. Toward this end, they are studying the permanent magnet that combines samarium with cobalt. These strong permanent magnets are similar in strength to neodymium magnets, but they can withstand higher temperatures and have higher coercivity. However, they are brittle and prone to cracking and chipping. The Livermore quantum-mechanical model computationally reproduces the properties of this magnet and gives researchers confidence as they search for solutes that could further improve the technology.

One goal of this effort is to partially substitute cobalt, a material sensitive to market price swings, with iron. The


Livermore researchers Patrice Turchi (foreground) and Scott McCall review the phase diagrams of aluminum–cerium–silicon and cobalt–iron–samarium alloys. Quantum-mechanical simulations and thermodynamic modeling are used to estimate the phase stability, magnetism, and other properties of potential rare-earth alloys. (Photo by Lanie L. Rivera.)

Livermore model has predicted the ideal mixture of iron and cobalt for maintaining the desirable properties of high-temperature and magnetic stability. "If stable, the material created from combining the rare earth samarium and iron could have fantastic properties," says Turchi. "We may want to add other rare earths as well as transition metals to fully stabilize the materials." For structural applications, thermodynamic modeling has been successfully used to optimize alloy composition in materials combining aluminum and cerium with other solutes. These models are helping guide the experimental efforts being conducted at Oak Ridge and Livermore.

## Lighting the Way

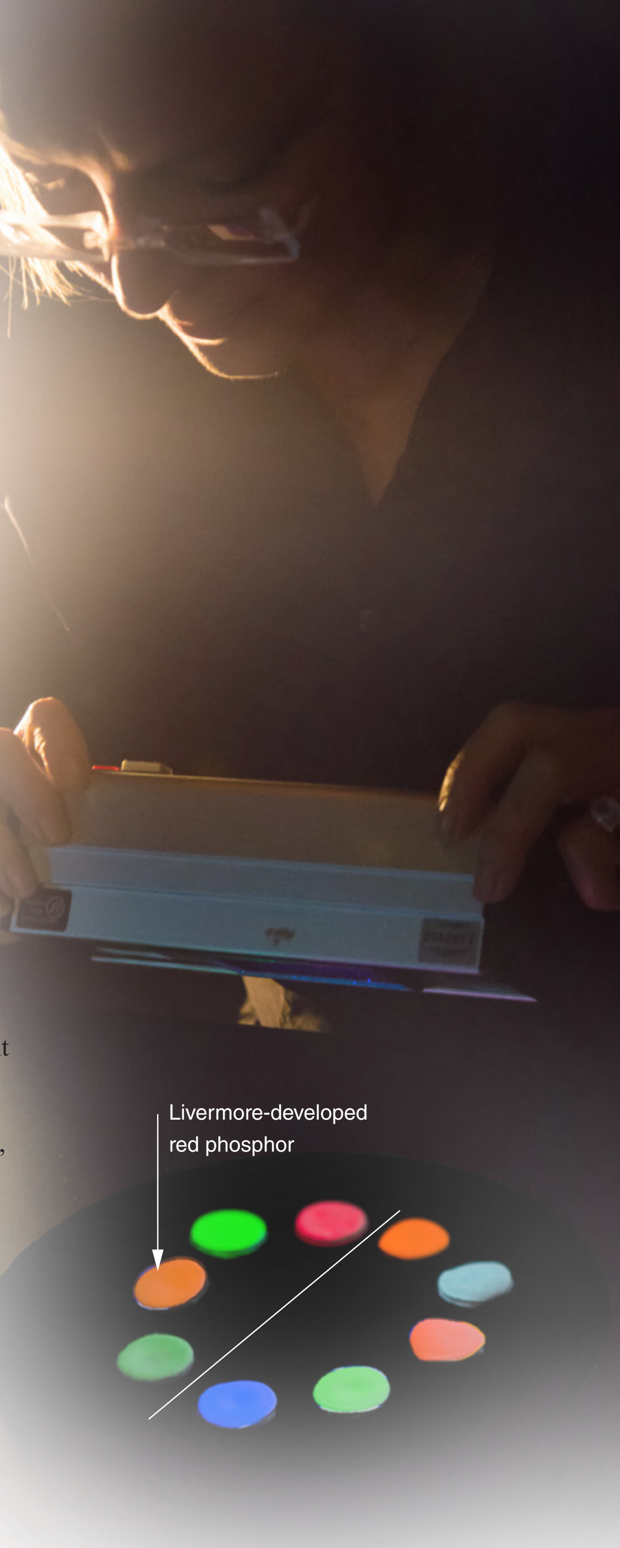
Advanced lighting systems are another technology that could benefit from rare-earth substitutes. Livermore researchers Steve Payne, Nerine Cherepy, Daniel Aberg, and Fei Zhou are working with colleagues from GE, Ames, and Oak Ridge to sharply reduce the rare-earth content of the three phosphors used in fluorescent lighting. Other Livermore team members include Zach Seeley, Kiel Holliday, Nick Harvey, Paul Martinez, Ich Tran, Alex Drobshoff, and several college summer students.

Current phosphors in fluorescent lighting consume more than 1,000 metric tons of rare-earth oxides yearly. GE, a major manufacturer of fluorescent lamps, has set a goal of reducing the quantity of rare earths in lighting by at least 50 percent without compromising the quality of the light or increasing the cost.

Cherepy and Payne explain that inside fluorescent bulbs electrons collide with atoms of mercury vapor. The excited mercury atoms emit energy in the form of ultraviolet photons (invisible to human eyes), which interact with three fluorescent phosphors coating the inside of the bulb. The current tri-phosphor blend uses a mixture of blue, green, and red light emitters that combine to produce white light. Fluorescent lamps contain critical rare-earth elements europium and terbium in their phosphors along with the lower cost rare earths yttrium and lanthanum. The blue phosphor has inherently low rare-earth content and therefore does not need to be replaced. However, europium and terbium are in high demand and eliminating them in the green and red phosphors would help stabilize the future cost of fluorescent lighting.

Any replacement phosphors must also sustain the color temperature (desired whiteness), lifetime (about 15,000 hours), and brightness of existing lighting. Further, the processing of the new phosphors must be compatible with current manufacturing infrastructure. GE scientists have identified a replacement green phosphor that reduces the terbium content by 90 percent and eliminates lanthanum entirely. Livermore researchers, responsible for reformulating the red-light emitting phosphor, have developed a compound of aluminum nitride doped with manganese. This phosphor is rare-earth free, eliminating both europium and yttrium oxides, and its light emission is close to the required wavelength of 610 nanometers.

In creating the new phosphor, the Livermore team began by reviewing scientific literature and searching spectral databases for emitters at the right wavelength. They then produced a small amount of candidate phosphors and tested them to determine their performance. In addition, physicists Aberg and Zhou performed quantum simulations of the prospective phosphors to calculate the substances' emission energies and various oxidation states. Much of their




Scientist Nerine Cherepy illuminates phosphor samples under ultraviolet light. Standard phosphors used in fluorescent lightbulbs (bottom right) could soon be replaced with those being developed by Livermore and collaborators that contain little or no rare-earth elements (top left). The Livermore-developed red phosphor is rare-earth free (Photo by Lanie L. Rivera.)

focus was on compounds containing manganese dopants.

Cherepy points out that the original phosphor used in fluorescent bulbs was a mined mineral, willemite, which is naturally doped with manganese. Several decades later, in the 1970s, rare earth–containing phosphors became the standard. Aberg explains that depending on their oxidation state, manganese ions exhibit different colors and are often used as pigments. "Manganese is a versatile dopant," he says. "We focused on finding a host for manganese that allows the element to emit red in a phosphor."

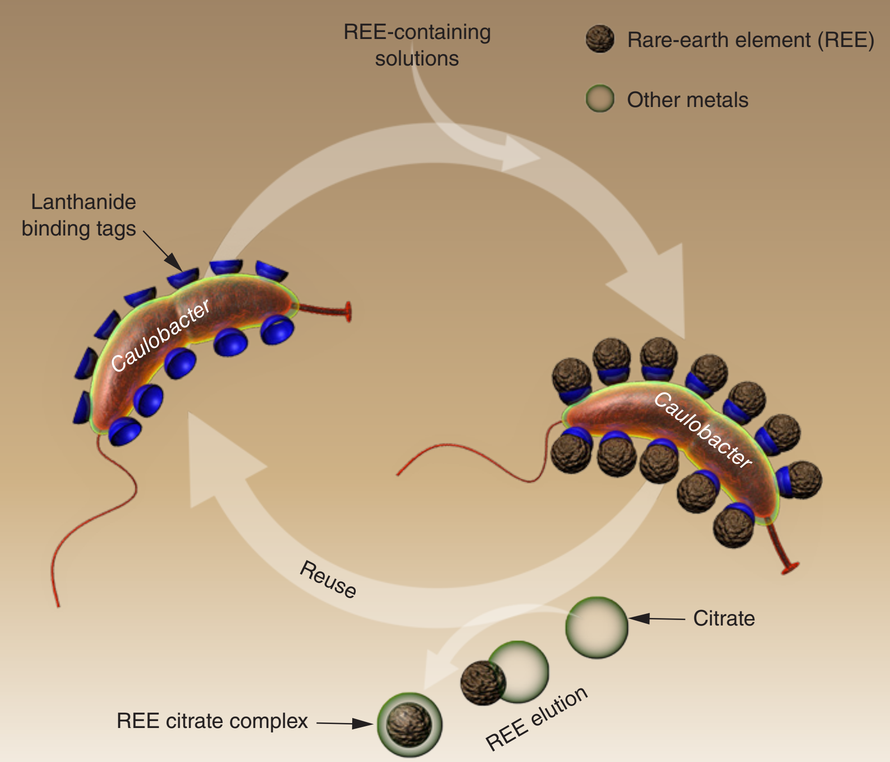
Work is still underway to ensure the commercial feasibility of producing fluorescent lighting using these phosphors, but the future prospects look good. "The fundamental physics of the green phosphor being developed by GE as well as Livermore's red aluminum nitride–manganese phosphor is compelling," adds Payne. "We are taking the next steps in advancing this research by evaluating chemical issues such as slurry compatibility, improving procedures to synthesize the elements, and refining cost estimates."

## Bacteria Create a Sticky Situation

The increasing demand for rare earths in emerging clean-energy technologies has triggered an urgent need for new approaches to efficiently extract these materials from ores and recyclable products. Livermore staff scientist Yongqin Jiao and colleagues are leading a project to develop a bioadsorption strategy for rare-earth recovery using genetically engineered bacterium.

*Caulobacter crecentus* is a common bacterium found in soil and lakes. (See *S&TR* April/May 2014, pp. 13–16.) The research team's genetically engineered *C. crecentus* has lanthanide binding tags attached to its outer cell wall. The tags have molecules called ligands that bind to metal atoms with 1,000 times greater affinity for rare earths than other metals. They also have an adsorption preference for heavy rare-earth elements relative to light elements.

An urgent need exists for new approaches to efficiently extract and recover rare-earth elements from ore and recyclable products. Toward this goal, Livermore scientists have genetically engineered the bacterium *Caulobacter crescentus* to adsorb rare earths onto its cell surface. The adsorbed elements can be recovered using citrate solution and the bacteria can be reused. (Rendering by Adam Connell.)

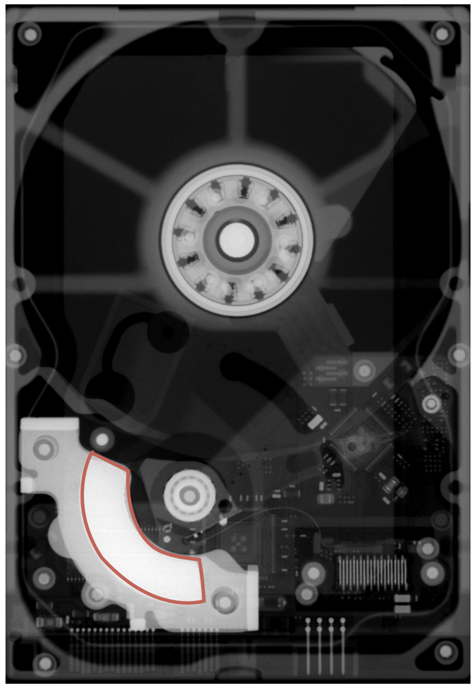


The rare earths adsorbed by the bacteria can be washed off with a solution of citrate (a derivative of citric acid). In addition, citrate is harmless to the bacteria so it can be reused many times. “Our results have demonstrated a rapid, efficient, and reversible process for rare-earth adsorption with potential industrial applications,” says Jiao, who adds that the novel technique would be applied mainly to low-grade waste material left over from mining. The rare earths would be leached from mine tailings, and the engineered bacteria would be added to the slurry to extract all the rare earths.

## Extraction and Retrieval

If discarded materials can be mined for their rare-earth content, these materials can also find new purpose. For example, magnets in computer hard drives are made with neodymium. Data centers for companies like Google and Amazon.com use millions of hard drives per center. Industry practice suggests one-third of hard drives be retired and recycled yearly to ensure data integrity, making them an ideal source for rare-earth retrieval.

Researchers Karina Bond, Jeffrey Kallman, William Brown, and Harry Martz are developing a method to automate the recovery and recycling of neodymium–iron–boron magnets from discarded computer hard drives. Bond’s prototype test bed for the method subjects hard drives to 160-kiloelectronvolt x rays, similar to those used in airport x-ray scanners. The magnets can be easily seen on the recorded x-ray images. Unfortunately, the magnets are located in different places depending on the hard drive. In addition, their size and shape can vary from one manufacturer to another. To facilitate an automated “punch” mechanism for extracting the magnets, machine-vision techniques are applied to locate their position and shape from the x-ray images. Bond says, “We need to demonstrate we can achieve a processing throughput of greater than 100 hard drives per hour to make this method economically feasible.”



An x-ray radiograph of a hard drive shows the rare earth–containing motor magnet outlined in red. X-ray images such as the one shown here are part of a Livermore-developed method to automate the recovery and recycling of magnets from discarded computer hard drives.

Once extracted, a magnet could be reused in its entirety or chemically processed to recover just the neodymium. Oak Ridge is responsible for developing methods to extract magnets given their location in the drives. Scientists at the Colorado School of Mines and Ames Laboratory are researching chemical processing methods to recover the rare-earth elements from the extracted magnets. Co-locating this type of magnet-extraction machine with data centers would eliminate logistics and supply chain challenges for rare-earth recycling. One idea is to design and install such a machine in the back of a truck for processing discarded hard drives at various server farms.

## Promoting Research Success

In addition to coordinating CMI-funded research at the Laboratory, Schwegler also leads CMI’s cross-cutting initiatives. This work, which involves researchers at eight different institutions, focuses on developing tools and techniques that are useful in three areas: enabling science, environmental sustainability, and supply chain and economic analysis. By creating validated predictive simulation tools and materials databanks, conducting environmental impact assessments of new technologies and strategies for mitigating deleterious effects, and evaluating supply chain and future materials criticality issues, cross-cutting research enables CMI’s overarching goal to diversify supply, develop substitutes, and reuse and recycle rare earths.

As demand for rare earths continues to grow commensurate with growth in clean-energy technologies, Livermore’s support of CMI and its critical materials research is ever more important. For the U.S. clean-energy industry, the payoff is reduced negative effects from a supply disruption and strengthened assurance of new products and technologies.

*—Arnie Heller*

**Key Words**: Ames Laboratory, *Caulobacter crecentus*, cerium, clean energy, cobalt, Critical Materials Institute (CMI), exchange spring magnet, fluorescent lighbulb, neodymium, phosphor, quantum mechanics, rare-earth element, samarium.

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